

**Proposal for Testing and Validation of Vacuum Ultra-Violet Atomic Laser-Induced
Fluorescence as a Method to Analyze Carbon Grid Erosion in Ion Thrusters**

Summary of Research Report

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January 1, 2003 – December 31, 2003

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NAG3-2822

Background:

Previous investigation under award NAG3-2510 sought to determine the best method of LIF to determine the carbon density in a thruster plume. Initial reports from other groups were ambiguous as to the number of carbon clusters that might be present in the plume of a thruster.¹ Carbon clusters would certainly affect the ability to LIF; if they were the dominant species, then perhaps the LIF method should target clusters. The results of quadrupole mass spectroscopy on sputtered carbon determined that minimal numbers of clusters were sputtered from graphite under impact from keV Krypton. There were some investigations in the keV range by other groups that hinted at clusters, but at the time the proposal was presented to NASA, there was no data from low-energy sputtering available. Thus, the proposal sought to develop a method to characterize the population only of atoms sputtered from a graphite target in a test cell.

Most of the ground work had been established by the previous two years of investigation. The proposal covering 2003 sought to develop an anti-Stokes Raman shifting cell to generate VUV light and test this cell on two different laser systems, ArF and YAG-pumped dye. The second goal was to measure the lowest detectable amounts of carbon atoms by 156.1 nm and 165.7 nm LIF. If equipment was functioning properly, it was expected that these goals would be met easily during the timeframe of the proposal, and that is the reason only modest funding was requested. The PI was only funded at half-time by Glenn during the summer months. All other work time was paid for by Whitworth College. The college also funded a student, Charles Shawley, who worked on the project during the spring.

The technical paper resulting from this work that was presented at the 2003 Joint Propulsion Conference² has been attached as an appendix to this report.

Experimental Results January 1, 2003 – December 31, 2003

Four different designs of anti-Stokes Raman shifters (SARS) were developed during the spring and summer. The final design followed the basic concepts of that used by the Dobeles group,³⁻⁴ but with the advantage that the lengths of each arm could be easily adjusted allowing for a variety of different focal optics to be tested for optimization. The center of the cell is kept at liquid nitrogen temperatures by a cold finger to optimize the shifting, as shown in figure 1. The entire device is constructed from stainless steel with brass window mounts. The final cell is shown in figure 2.

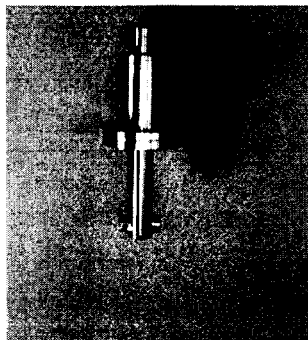


Figure 1 – The cold finger

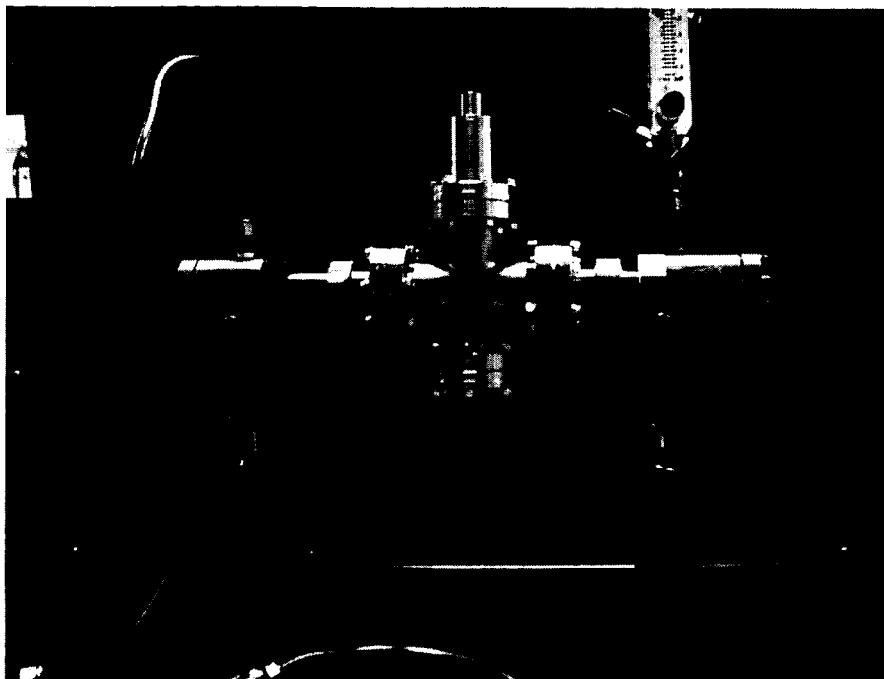


Figure 2 – Assembled anti-Stokes cell

ArF System:

The 193 nm 750 Hz ArF laser seemed promising for producing 156.1 nm light. However, the system never produced stable output in the anti-Stokes region. Many methods were tried to improve the power and stability. These included the construction of a 1 meter long Stokes cell to precede the anti-Stokes cell for seeding and the use of a variety of optical configurations. A possibility considered was that some of the optics were not transparent enough at 156.1 nm and may be absorbing light, so the laser gas was changed to KrF which produces light at 248 nm. With KrF, it was assured that the first three anti-Stokes lines would have a wavelength greater than 193 nm and would be transmitted by the optics. KrF did yield a weak and unstable first-order shift that disappeared at higher repetition rates, much like the ArF laser.

YAG-pumped Dye Laser System:

Based on the work of the Dobeles group and the laser manufacturer's specifications, it was anticipated that the system detailed in the JPC technical paper² would produce an output of 60-90 microjoules at a 20 Hz repetition rate, which would detect carbon atoms at a much lower threshold than previous groups. The new laser system was to be provided by Pacific Northwest National Laboratories (PNL). The new laser system (Spectra Physics Sirah dye laser) was late in shipping to PNL and did not arrive until July. It was operating to specifications in August; however, after approximately a week of operation, the prisms in the dye laser became burned. It appeared obvious that the half-dozen prisms involved were defective, since traditionally more sensitive items such as beam splitters were unscathed. A repair call was made to the manufacturer, who sent a technician with new prism in November to repair the dye laser. Within a day of

operation, the prisms burned again and the laser was unusable. In the meantime, the anti-Stokes cell was tested at 355 nm with the functional equivalent amount of light as the anticipated 12 mJ from the dye laser at 209 nm. Using this 355 nm light, the requisite 3 orders of shift were observed from the anti-Stokes cell. This demonstrated that the anti-Stokes cell was functional.

LIF results:

Since neither method produced the requisite VUV light, the detection limits were not able to be determined. Since the experimental apparatus is in place, the PI expects to make this measurement, funded by the college and PNL, the moment the dye laser becomes functional.

Other qualitative results:

Over the three year period of this investigation, Whitworth College has benefited greatly from this collaboration with NASA. Collaborations with the Pacific Northwest National Laboratory arose as a direct result of this award. In addition, over the past three years four students gained valuable research experience working on this project: Charles Shawley, Ashley Hamilton, David Clark and Ben McDonald.

Conclusion:

A number of different configurations were attempted to try and achieve 156.1 nm and 165.7 nm laser light. A number of technical difficulties, particularly the failure of a laser to perform as advertised, prevented the determination of the number density of carbon atoms sputtered by Kr ions. Once the laser is functional, the data will be gathered even though the grant period has ended. At that point, I plan to write up the results and submit a paper to *Nuclear Instruments and Methods B*.

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¹Abdullaeva, M. K., Atabaev, B.G., and Dzabbarganaov, R., "Neutral and Negative Ion Cluster Emission During Sputtering," *Nuclear Instruments and Methods in Physics Research*, **B62**, 43-46, 1991.

²R. E. Stevens, "Detection Limits for a VUV Erosion Diagnostic for Carbon Grids" AIAA 2003-4562 39th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, **2003**.

³Bogen, P., Dobelev, H. F., and Mertens, Ph., "Measurement of Velocity Distributions of Sputtered Carbon Atoms Using Laser-Induced Fluorescence in the Vacuum UV," *Journal of Nuclear Materials*, **145-147**, 434-437, 1987.

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DETECTION LIMITS FOR A VUV EROSION DIAGNOSTIC FOR CARBON GRIDS

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ABSTRACT

Laser-induced fluorescence (LIF) has shown promise to rapidly measure erosion of molybdenum and titanium thruster grids *in situ*. Atomic carbon transitions occur in the vacuum-ultraviolet region not readily accessible by commercial lasers. A laser system using anti-Stokes Raman shifting in hydrogen to produce 156.1 nm laser light is currently under development. Characteristics of this laser system will be presented along with the detection limits for carbon atoms in the plume of an ion thruster.

INTRODUCTION

Carbon graphite and carbon-carbon composite^{1,2} have been shown to have superior erosion resistance compared to molybdenum grids; thus, carbon shows promise for increasing the longevity of electric propulsion systems. A real-time *in situ* erosion diagnostic for molybdenum with an absolute density calibration is currently under development at NASA Glenn Research Center.³⁻⁵ A similar diagnostic for carbon-based grids would allow for rapid erosion-testing of carbon grids as well as direct comparison with molybdenum grids.

For molybdenum thruster grids, the erosion product is primarily ground-state molybdenum atoms.⁶ The density of molybdenum atoms in the thruster plume can be measured by laser excitation^{4,7} at 345.6 nm followed by fluorescence emission at 550.6 nm. Atomic carbon transitions suitable for LIF are much more difficult to reach than is the case for molybdenum. Molybdenum starts to have suitable transitions⁶ in the UV at 390.2 nm, which is comfortably within the reach of a frequency-doubled dye laser; the first accessible carbon transition is 165.7 nm, well beyond the reach of simple commercial laser systems. The best methods of reaching these transitions by laser is either Raman shifting a UV laser beam⁸ or frequency tripling a laser beam in a xenon gas cell.⁹ Neither process is efficient, producing little power of the desired frequency. However, each referenced technique has been exploited to measure carbon sputtering by groups interested in erosion processes in Tokamak-type reactors.

A stumbling block in the development of a carbon erosion diagnostic has been the ambiguity regarding

the amount of carbon clusters sputtered compared with single atoms. For refractory metals, single atoms are clearly the dominant species. For carbon materials, the case is much less clear. In order to develop an absolute calibration, the relative proportion of carbon clusters sputtered must be determined. It is likewise important to know the ratio of ejected species in order to assess the absolute lower limits of detection in the plume of a thruster.

This paper describes the ongoing work in characterizing a VUV LIF system for the purpose of developing an erosion diagnostic. The relative sputtering of clusters will be addressed and the experimental setup for the VUV LIF will be presented.

RELATIVE PROPORTION OF CLUSTERS SPUTTERED FROM CARBON

With number densities of sputtered species in the ion plume close to the absolute limits of LIF detection, determination of the relative proportion of clusters sputtered from graphite is important in terms of determining the feasibility of a carbon LIF diagnostic as well as accurately calibrating that diagnostic. Most of the measurements of the relative cluster yield have occurred in the keV range and only recently have groups begun to examine the 100 eV sputtering regime which more accurately simulates erosion of ion accelerator grids by charge exchange ions.^{10,11} Table I summarizes the work of several groups.

With the exception of one very recent work,¹⁴ all of these studies have been conducted in the keV range and show carbon clusters as a minority sputtered species. Lacking data in the lower energy range, we designed an apparatus to try and determine if cluster proportion

Table 1 – Summary of Cluster Sputtering Data for Carbon

Projectile	Group	C2/C1	C3/C1	Technique
5 keV Ne+	Vietzke[12]	0.054	0.016	TOFQMS
5 keV Ar+		0.056	0.030	
2.5 keV Cs+	Abdullaeva[13]	0.1	0.02	SNMS
1.5-3keV Kr+	This work	<0.05	<0.02	QMS
10-200eV Xe+	Doerner[14]	10	?	Spectroscopy
Laser Ablation	Meyer[15]	1.4	17	TOF
Thermal Equil.	Drowart[17]	<1	>1	TOF

increased significantly as energy decreased. This apparatus consisted of a VG Scientific EX-03 ion gun capable of producing a beam of noble gas ions from 500 eV to 3 keV. The ion gun targeted a rigid graphite target (Goodfellow, 99.95% pure) placed 8 cm from the ion gun. A Merlin 100 MHz quadrupole mass spectrometer(QMS) was used to detect sputtered species. The system was pumped by a Leybold hybrid turbo pump; when the ion gun was not operating, chamber pressures were in the 10^{-10} Torr range (after bakeout). While operating, the background pressure was kept in the 10^{-6} torr of Kr (99.999% pure) from the ion gun inlet. This provided ion beams of 10-20 μ amps depending on the ion energy.

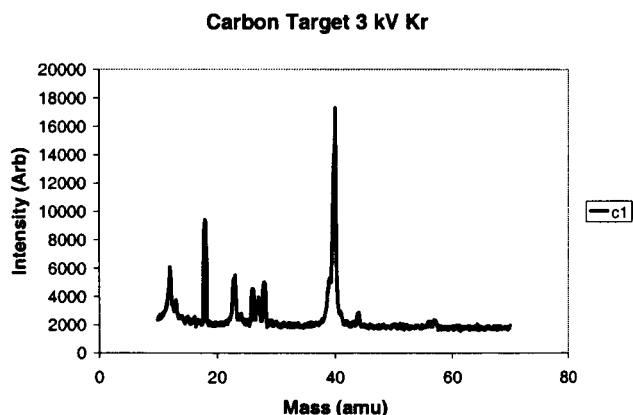


Figure 1 – Mass Spectrum of sputtered graphite

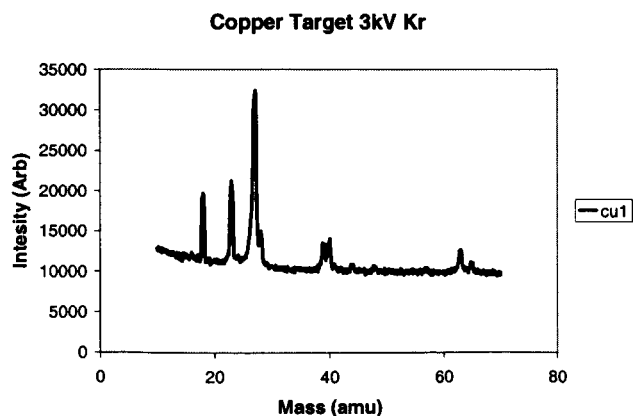


Figure 2—Mass Spectrum of sputtered copper

Contamination from other carbon species proved to be a serious initial problem. The quadrupole uses an electron impact ionizer to detect neutral species and, as per Meyer,¹⁵ it was found that setting the electron energy above 20 eV resulted in a large carbon signal from the cracking of other carbon-containing molecules. Indeed, the carbon atom signal did not change regardless of the target when the electron impact was 100 eV. Data collected with an electron impact energy of 18 eV (following a reference for laser ablation¹⁵) provided reliable data as shown in figure 1. A copper target was used as a reference as shown in figure 2. From the range of impact energy of 3 keV to 1.5 keV of Kr ions, no substantial amount of C₂ or C₃ was detected. Because the ionization efficiencies are not known, and estimates vary,¹² this data indicates that C₂ and C₃ are sputtered less than 5% and 2% of the time. Meyer's estimates¹⁵ of relative ionization cross-sections at 18 eV for C₁:C₂:C₃ as 1.00:0.90:0.82 were used along with the relative electron multiplier yields of 1.00:0.71:0.58. This 5% and 2% limit is consistent with higher energy studies.¹² Below 1.5keV ion energies, the ion beam became wider than the target and contamination from sputtering the sidewalls and mount made cluster composition ambiguous.

LIF FOR ATOMIC CARBON

Based on the 8200 hour wear test,⁴ the maximum calculated Mo density on centerline is 5×10^8 atoms/cm³. Data are not available for the number density downstream of a carbon grid thruster. It is expected that carbon erosion will be significantly less than molybdenum erosion in any given thruster design. In addition, clusters produced during sputtering will no doubt reduce the effective number density of atoms in the plume of an ion thruster. The possibility of cluster LIF has been discussed in previous work.¹⁸

Other authors^{8,9} have used LIF to measure both densities and velocity distributions of sputtered atoms from graphite and TiC. Two separate techniques were tried by those researchers. Frequency tripling in a xenon gas cell⁹

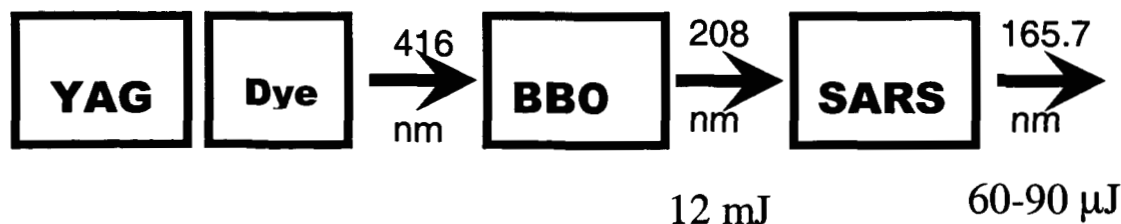


Figure 3 – Diagram of VUV Laser System

produced 200W (0.8 μJ energy in a 4 ns pulse) output from a 4 MW input pulse at the carbon lines at 115.8 nm and 127.7 nm. This power was not enough to saturate either transition. The authors estimated the detection limit of carbon atoms in their specific experimental arrangement to be 2×10^8 atoms/ cm^3 . The second method¹⁰ involved the 8th order anti-Stokes Raman shift (SARS) of 4 MW of 368.8 nm light to produce approximately 500W (2 μJ energy in a 4 ns pulse) at 165.7 nm. The method of calibration was a glow discharge in CO; however, CO produces interfering fluorescence at this wavelength, obscuring the carbon atoms. An attempt was made by these authors to use the 9th order anti-Stokes Raman shift to reach the 156.14 nm carbon line, but the output proved too unstable to produce reliable results. The authors of these works did not account for the possibility of cluster emission from sputtering, photodissociation of C_2 by the vacuum UV light, or the absorption bands of C_3 in the VUV region.

More recently,¹⁹ the authors of the previous works have moved to a system that doubles a dye laser output to produce 4-8 mJ of light in the 225-230 nm range. This light is then anti-Stokes shifted to produce 10 μJ of light in the 150-160 nm range. This appears to be more stable than the previous systems.

For carbon thruster LIF, an anti-Stokes system that will provide superior VUV light will be developed as shown in figure 3. A Spectra-Physics Sirah Dye Laser (Model #PRSC-G-24) dye laser using Excalite 417 dye pumped by 355 nm Spectra Physics PRO-270-20 YAG laser will produce 126 mJ of 418 nm light, which can be frequency doubled to produce 12 mJ of 209 nm light. This should be superior in energy output of each shift compared to the energy output from 4-8 mJ of 230 nm light used by previous groups.¹⁹ In addition, only 3 shifts are required to reach the 165.7 nm carbon line (4 shifts of 211 nm light will reach the 156.1 nm carbon

line.) Each higher order shift scales the energy by a factor of 0.3, so the reduction in order will be significant in increasing the power by a factor of 3. A final output energy of 60-90 μJ per pulse on the atomic carbon line is expected at a 20 Hz repetition rate. This increase in power and stability should significantly lower the detection threshold below the level determined by previous groups of 2×10^8 cm^{-3} using approximately 1 μJ of pulse energy.

The LIF system detection limits will be tested in a small sputtering chamber shown in Figure 4. An EX-03 Ion Gun will sputter a graphite target with up to 20 μamps of Kr or Xe ions in a 1 cm diameter target. This will provide a maximum C atom density of 2.5×10^9 cm^{-3} near the surface of the graphite target. This density can be lowered to the 10^7 cm^{-3} level, which would correlate to the expected plume density for an NSTAR type thruster using carbon ion optics, simply by reducing the output of the ion gun. The laser beam will pass over the carbon sample parallel to the carbon surface. Light is gathered at 90° to the laser beam by CaF optics and detected by a solar blind Hamamatsu photomultiplier combined with a Stanford Research Systems gated photon counter. The entire optical beam path is vacuum or nitrogen purged due to the oxygen absorption of the VUV light.

CONCLUSIONS

The most viable option for carbon LIF appears to be anti-Stokes Raman shifting to the atomic transitions at 165.7 nm and 156.1 nm. Previous LIF work had determined a detection threshold of 2×10^8 cm^{-3} for sputtered atomic carbon. A laser system currently under development will provide superior energy and stability at the carbon lines and thus lower the threshold for detection to useful levels.

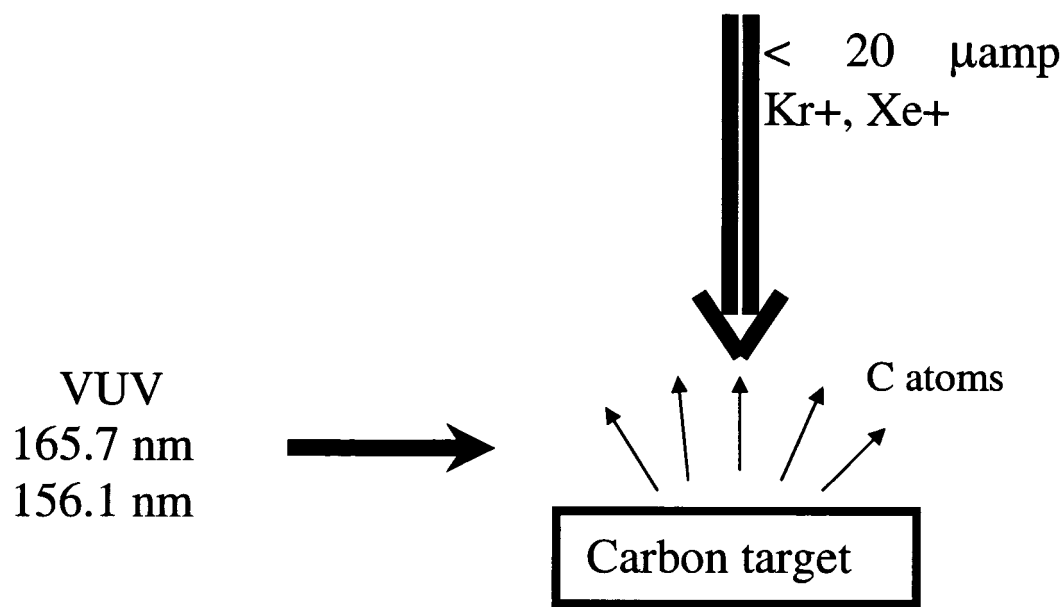


Figure 4 – Experimental Configuration for Testing the Detection Limits for Atomic C by LIF. The view is from the perspective of the photomultiplier (out of the page).

ACKNOWLEDGMENTS

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